University of Gondar

College of Natural and Computational Sciences

Department of Chemistry

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Identification and Spectroscopic Characterization of Natural Gem Agate from West Belessa, North Gondar, Ethiopia

By

Yenus Abubaker Fenta

Advisor: Walelign Wubet Melkamu (PhD)

A Thesis Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Chemistry (Inorganic)

Gondar, Ethiopia

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Thesis Approval Sheet

The thesis titled "Identification and spectroscopic characterization of natural gem Agate from West Belessa, North Gondar, Ethiopia" by Mr. Yenus Abubaker Fenta is approved for the degree of "Master of Science in Chemistry (Inorganic)".

Examiners

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I, the undersigned, declare that the work reported herein represents my own ideas in my own words and wherever others' ideas or words have been included, I have adequately cited and referenced the original sources. I understand that non-adherence to the principles of academic honesty and integrity, misrepresentation/fabrication/falsification of any idea/data/fact/source will constitute sufficient ground for disciplinary action by the University and can also evoke penal action from the sources which have not been properly cited or acknowledged.

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Acknowledgement

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Yenus Abubaker

June 2017

LIST OF ACRONYMS

α	**Alpha**
Ch	**Chalcedony**
FAAS	**Atomic Absorption Spectroscopy**
FT-IR	**Fourier transform infrared**
Mo	**Moganite**
Opal-CT	**Opal-Cristobalite, Tridymite**
RI	**Refractive index**
SG	**Specific gravity**
XRD	**X-ray diffraction**

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ABSTRACT

The sample of agate was recieved from Gondar Polytechnique College, Gondar, which is found in West Belessa, North Gondar, Ethiopia. To identify the silica phases present in the sample of agate that occur in West Belessa, X-ray diffraction (XRD) spectroscopy were performed. Fourier transform infrared (FT-IR) spectra of natural gem agate were performed to identify the nature of water present. Using Flame Atomic Absorption Spectroscopy (FAAS) technique the content of different element composition; (Ca, Fe, Cu, Mn, and Mg) was determined. In order to verify that the sample were indeed agate, some basic preliminary identifications using, a refractometer, heavy liquid method, and "MOHS HARDNESS PENCILS" were carried-out. The physical measurement shows that the hardness of the sample (6.5 to 7), the refractive index is (1.53 to 1.54), and specific gravity of (2.57 to 2.62). The results of the measured values are closely related to literature data which verifies the sample were indeed agate.

For FAAS trace element determination optimization are established by extensive testing of different parameters (temperature, time of drying, reagents volume ratio). It was observed that the white color of agate correlates with the presence of Ca in the sample. FT-IR spectra indicate the presence of both free molecular H_2O and defect site silanol Si-OH. X-ray powder diffraction studies of agate that occur in West Belessa shows, strong and moderately intense diffraction peaks for the overlap of α-quartz with that of moganite, and the lowest peaks corresponding to single α-quartz and moganite.

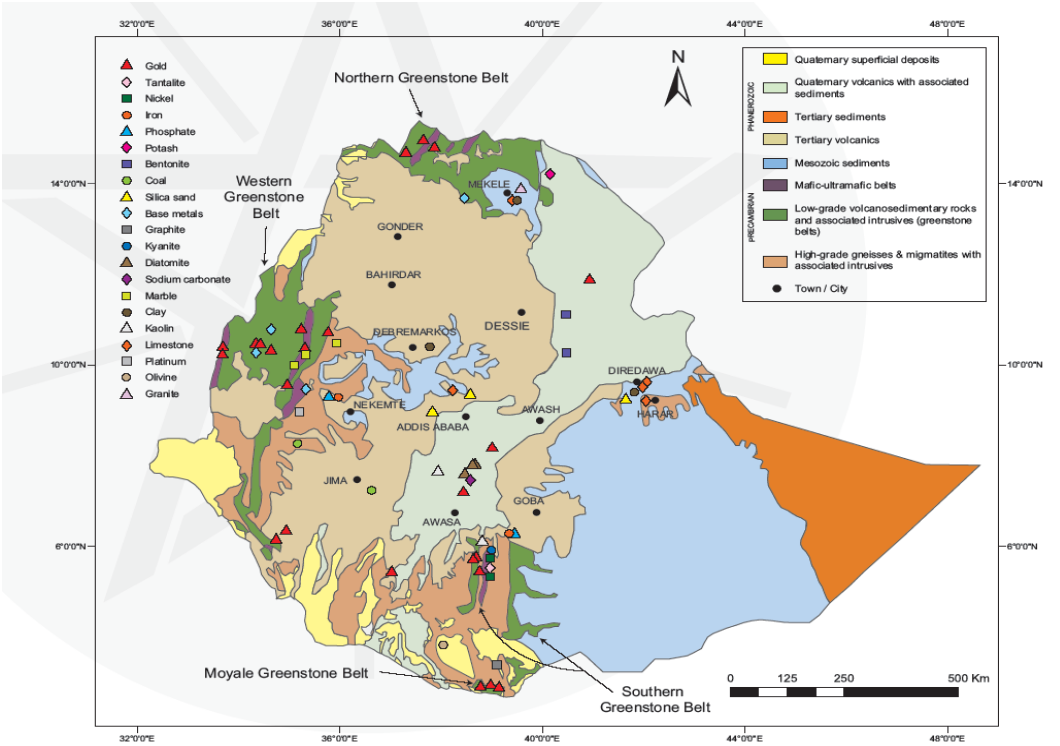
The characteristic of XRD and FT-IR spectral data for agate sample from West Belessa, North Gondar (Ethiopia) will have a significant contribution in their identification and characterization. The metals level observed in the sample are comparable with their corresponding worldwide reported values.

Key words: Gemstone; Agate; XRD; FT-IR; FAAS; West Bellesa; Ethiopia

1 INTRODUCTION

1.1 Background

Ethiopia is endowed with rich mineral resources and offers excellent opportunities for mineral prospecting and development. Favorable geological environment hosting a wide variety of mineral resources have identified by geological studies [1]. According to the Ministry of Mines and Energy, substantial gold deposits and more than 500 metric tons of gold deposits have already been identified in Ethiopia's green stone belts by Government exploration efforts. Additional reserves are expected to be identified in at least seven regions of the country. In addition to gold, there are good deposits of tantalum, platinum, nickel, potash and soda ash. Among construction and industrial minerals are marble, granite, limestone, clay, gypsum, gemstone, iron ore, coal, copper, silica, diatomite, etc. Geothermal energy also exists in good quantity.



Key mining operations and mineral deposits in Ethiopia
(information from the Geological Survey of Ethiopia and the Ministry of Mines and Energy)

Fig. 1. Key mining operations and mineral deposits in Ethiopia [2].

GEMSTONES

According to Geological findings potential sources of precious and semi-precious stones have identified in many parts of Ethiopia [3]. There is no doubt that Ethiopia has a vast mineral wealth. Granite, Marble, Sandstone and Limestone are also found in abundance all over the country. In Ethiopia, studies have so far shown that the following gemstones are found: Apatite, Almandine, Garnet, Amethyst, Aquamarine, Chalcedony, Chrysoprase, Citrine, Emerald, Garnets, Jasper, Obsidian, Peridot, Ruby, Topaz, Diamond, Sapphire, Sodumene, Tourmaline, opal and Agate.

Agate is microcrystalline quartz mineral, chalcedony variety, commonly used as semiprecious gemstones, ornamental objects and grinding media [4]. The price of the agate geode (unprocessed in its natural form) is fairly low. However jewelry artists can cut, polish and process the agate geode into many beautiful gemstones, and this process increase the value many fold. The most common agate with a simple processing like cutting and polishing can be in the range of US$ 2 per carat (200 milligrams), the more rare types like some specimens of fire agate, etc can fetch prices of more than US$20 per carat.

Agate is found in many parts of Ethiopia in volcanic and sedimentary environment, however little is known about mineralogy, element composition, and water contents present. To address this knowledge gap, this paper presents the application of FAAS, FT-IR, and XRD to determine the various trace elements present (Ca, Cu, Mn, Mg and Fe), to identify and characterize the type of water and the main silica building phases present in agate from West Belessa to discriminate other agates reported by different scientists in different countries (such as Turkey, Brazil, Chile. etc). Preliminary identification of the studied agate is performed using refractometer, Mohs hardness pencils and heavy liquid method.

1.2 The Chemistry of Agate

1.2.1 Formation and occurrence

Agate has very high silica purity containing < 1% non- volatile impurities. The major impurity with a concentration up to 2% is the total water (H_2O and Si–OH groups). However, most agate contains two silica polymorphs: Alpha (α)-quartz and moganite [5].

Agates most commonly formed in both SiO_2-rich (rhyolite, rhyodacite) and SiO_2-poor (andesite, basalt) volcanic rocks and associated with late or post-volcanic alteration or weathering of volcanic host rocks as believed by many authors. Less commonly, agates may also formed in fissures and fractures of crystalline rocks as hydrothermal vein agates, or in pores and cavities of sedimentary rocks from SiO_2- rich solutions at low-temperature [6].

Agate can be found all around the world and the classical agate countries are, Argentina, Brazil England, Germany, Mexico, Morocco, Uruguay, the U.S.A. (Oregon, Washington, Montana), Scotland and Turkey [7] but it can also be found in many other places. In Ethiopia, gemstones and semi-precious stones are apparently rare, and very few details are known about their occurrence. Nevertheless, minerals of gemstones (e.g. beryl, aquamarine, tourmaline, garnet, spinel, topaz, chalcedony and agate) are reported to occur in Sidamo (Kenticha, Kibre Mengist area), Harrar, Tigray (Axum and Adwa area: amethyst). The major occurrences are related to pegmatite–granite rocks. The gravels of some of the major rivers of Ethiopia host some secondary alluvial occurrences [8]. Despite the worldwide occurrence of agates and numerous investigations, the process of agate formation is not well understood. The source of silica from which agates are formed is one of the problems concerning agate genesis. In general, agates are formed either by hydrothermal activity of the silica originated in the host rock or surroundings, and was deposited in a gas vesicle or from lump of silica or gel that contains trace elements and water within the magma. During the alteration of the volcanic wall rocks the SiO_2 necessary for agate formation is mobilized by hydrothermal activity. Various silica minerals are precipitates from influxes of siliceous fluids with differing degrees of silica saturation and trace element concentrations; for example, low defect crystal quartz precipitates from water with relatively low silica concentration, while amorphous silica precipitates from water with high silica saturations [9].

One of the major depositional problem lies with the formation of the quartzine-chalcedony repeated bands, not the colored banding that can be seen with the naked eye. The silica necessary for agate formation most likely derives both from hydrothermal fluids and SiO_2 which was released during the alteration of unstable silicates and volcanic glass. For example, chemical weathering occurs by dissolution of potassium feldspar (fairly common silicate and can be found in igneous, metamorphic and sedimentary rocks) releases silica according to the Equ. (1) and dissolved by the groundwater in accordance to Equ. (2)

$$\mathbf{2KAlSi_3O_8 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2KOH + 4SiO_2} \quad \text{.....Equ. 1}$$

$$\mathbf{SiO_2 + 2H_2O \rightarrow H_4SiO_4} \text{ (monosilicic acid)} \quad \text{.....Equ. 2}$$

The pH of circulating fluids increased by the contents of alkaline-earth elements (MgO, CaO) and alkaline elements (Na_2O,K_2O) in leachates, and by the released KOH promotes the dissolution and diffusion of silica in the form of ionized silicic acid [$Si(OH)_4$] and enters in to the vesicles. Once the silica is in solution and upon an increase in concentration for example by evaporation, the silicic acid that diffuses into the vesicles slowly polymerizes [10]. This is how it happens:

$$\mathbf{\equiv Si\text{-}OH + \equiv Si\text{-}OH \rightarrow O\text{-}Si\text{-}O + H_2O} \quad \text{..... Equ. 3}$$

The polymerization of silica in solution loses Si and gain water. In the course of time at low temperature, even partial polymerization is no longer sustained, and the remaining monomeric silica leads to the crystallization of perfect quartz crystal. Thus, chalcedony-quartz repeated bands (Fig. 3A) that is typical of agate represents transformation from partially polymerized silica solution to non polymerized fluid, and the repeated chalcedony-quartz textures suggest successive in filtration partially polymerized silica [11]. Because this crystallization rate is slow, silica loss near the growing crystal face is eventually overrun by diffusion of silica toward the fiber tips, and the local activity of silica in solution increases. When polymerization is tenable again, the spiral growth mechanism is reactivated and rapid crystallization of defective chalcedony continues [12]. That's why an agate may be its banding pattern.

It is difficult to estimate the temperature of agate genesis, but the physiochemical process responsible for agate formation must take place in a low pressure/ temperature range which is below 200^{o}C and silica is transport through the host rock as silicic acid $Si(OH)_4$. Under alkaline

conditions, fibrous quartz (agate or chalcedony) could survive at low pressure and a temperature of < 300^{o}C. The most widely accepted temperature of agate formation as believed by many authors is that genesis starts with polymerization of siliceous fluids at temperatures ≈100^{o}C. Firstly, agates are deposited from silica solution in water approximately ≻ pH 7. Depending on the pH and temperature, the monomers of silica in water solution are $Si(OH)_4$ and poly nuclear complexes. At pH greater than 9.5, charged silicate monomers also come into consideration. Dissolved Si is present as mono silicic acid at the values of pH < 9.

In general, formation of agate takes place only in alkaline solution and low Pressure–temperature conditions (pH 8–9, about 90–150^{o}C, and near surface pressure) then the monomers of silica in water solution ($Si(OH)_4$) forming agates precipitate in to the open cracks directly and/or closed cavities by diffusion [13].

1.2.2 General properties of natural agate

Characterizing minerals by main physical properties in general and agate in particular include crystallography, hardness, color, cleavage, specific gravity, and refractive index.

A) Crystallography

Agate is not a homogeneous material that contains a single crystal α-quartz; it also contains tetrahedrally coordinated silica polymorph called moganite [5].

Alpha quartz consist hexagonal (six member ring) corner sharing SiO_4 tetrahedra so that each Si is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms. The resulting structure forms an open three-dimensional framework, so that quartz is classified as framework silicate. The crystal system is trigonal with unit cell parameters a = 4.9137 Å, b = 4.9137 Å and c = 5.4047 Å, Z (Number of formula units per cell) = 3. The structure is a centric, so exists in right and left-handed enantiomorphs. The space group of right handed is $P3_121$ while $P3_221$ is left handed [11].

Moganite is another silica polymorph that often forms an intimately intergrowth with α-quartz in many microcrystalline SiO_2 varieties. The structure of moganite is distorted four-member ring of corner sharing SiO_4 tetrahedra in three-dimensional framework [14]. The crystal structure is an alternate stacking of layers of left and right-handed quartz at the unit-cell scale. Moganite is monoclinic with the cell parameters a = 8.75 Å, b = 4.87 Å, c = 10.71 Å, β = 90.09°, Z (SiO_2) = 12, Density = 2.55 g/cm^3 [15].

The structure of agate can be probably interpreted as alternating formation of cryptocrystalline α-quartz called chalcedony intergrowth with cryptocrystalline quartzine called moganite (Mo), and crystalline low defect α-quartz (Fig. 2.A). These bands comprise layers with distinctly different grain sizes and defect concentrations. The diameter of crystalline low defect α-quartz zone measures 10 – 100 nm, while the cryptocrystalline α-quartz with moganite zone measure a diameter of 5 – 10 nm [12].

B) Hardness

The resistance which a mineral offers to abrasion or scratching is called hardness. In this manner minerals are tested and arranged based on their hardness. To fix the hardness of minerals a scale of hardness in ascending order has been devised, known as Mohs scale of hardness [16] which is given below: The hardness of agate is 6.5 to 7.

Table 1. Mohs scale of hardness of minerals

Minerals	**Hardness(Mohs scale)**	**Minerals**	**Hardness(Mohs scale)**
Talc	1	Feldspar (Orthoclase	6
Gypsum	2	Quartz	7
Calcite	3	Topaz	8
Fluorite	4	Corundum	9
Apatite	5	Diamond	10

C) Color

Agate can be of any color, the most frequent colors are gray, white, brown, salmon, red, orange, black, and yellow. Shades of violet and blue tons are very rare. The variation of colors depends on the species and concentration of trace elements. Agates thus can provide direct visual evidence for correlations in concentrations among trace elements and between trace element concentrations and color contrasts. For example, yellow- red colors of agate is caused by iron oxide and hydroxide coloring agent. Traces of manganese and nickel oxides produce the rarer agate colors of green and yellow. Agate's common white bands consist of nearly pure silica. Due to its porous nature, it is often dyed artificially to get black, red green or blue to make them more colorful and more eye-catching.

D. Cleavage

This is related to the internal crystals structure and forms an important character. It is the property of easily splitting or separating along definite planes, known as the cleavage planes. Crystals of different minerals have different degrees of cleavage; therefore it is important in determining minerals. 'Perfect', 'imperfect', 'distinct' or 'indistinct' are the different degrees of cleavage. Cleavage is also a property usually taken advantage of in cutting gem-stones. Cleavage is not related to hardness and is possessed by both soft and hard minerals. Natural agate has no cleavage**.**

E) Specific Gravity (SG)

Specific gravity, also known as relative density, widely differs among gemstones, and is one of their most important physical characteristics from gem identification point of view. Specific gravity (SG) is the ratio of the weight of one unit volume of the gem to the weight of the same unit of water. The SG of agate is (2.57-2.62).

F) Refractive index (RI)

Refractive index, n, of a material can be expressed as the ratio between the velocity of light in the air (V) and its velocity in the denser material (v), that is, n = V/v [17]. As basis for comparison the velocity of light in air is considered equal to 1, n = 1/v or the refractive index is equal to the reciprocal of the velocity. The precise relationship of the angle of incidence (i) to the angle of refraction (r) is given by Snell's law which states that for two media the ratio of sin i: sin r is a constant. This is usually expressed as sin i/sin r = n, where the constant n is the refractive index. With fixed frequency, the longer the wavelength, the greater the velocity. Red light with its longer wavelength has a greater velocity than violet light and because of the reciprocal relation between velocity and refractive index; n for red light is less than n for violet light. A crystal thus has different refractive indices for different wavelengths of light. The refractive index of agate is (1.53 to 1.54).

G) Uses and Application of agate

Agate has been found in the Omo valley in Ethiopia around 2.5 million years ago where our ancestor's made primitive stone tools like axes for them. Therefore, we can safely say that agate is not a recent discovery. Due to the materials hardness and ability to resist acids, agate is used to make mortars for powdering and mixing chemicals. It is also used for many other decorative

items though out the history, such as bowls, vases etc. and there exist thousands of beautiful objects in museums as well as with private collectors around the world.

Agate is the most beautiful and interesting gemstone in the jewelry industry because of its translucency, wide range of colors and most importantly, it's distinctive banding patterns. By cutting and processing agate in to jewelry gemstones, an incredible range of products can be made.

1.3 Research Purpose and Scope

Significance of the study

Basically, studies and research findings are intended to contribute some valid knowledge to the well being of the society and advancement of the society and studies on a gem stone is hoped to shape the gem trade by grading the gemstone.

In this regard, addressing the identification and characterization of gem agate as such studies could be useful to the gem importers, retailers, jewellery manufacturers, dealers and to the society. Identification and characterization of gem stone may be useful:

- To improve the awareness of the consumer on the fact that many varieties of gemstones on the market today have been treated or enhanced.
- To improve the understanding of the resource usage around the studied area.
- For appraisal and certification of gem stone in the studied area.
- To promote growth of mineral based sub sector of the country.

1.4. Objectives of the study

General objective

- To identify and characterize gem agate hosted in West Belessa using XRD, FT-IR and FAAS.

Specific objectives

- To determine trace elements of agate;
- To identify the type of water and silica polymorph present in agate and
- To identify the type of gem agate deposited in West Belessa in comparison with other localities.

Delimitation of the study

Study on identification and characterization of gem agate is difficult. It needs a careful investigation and takes long period of time and requires instruments like; Raman spectroscopy, ICP-MS, and SEM which are not available in our university. Moreover, to conduct the study on this particular area is too specific and too limited. The result that could be obtained from the study area, but which needed a survey of different area in the country, will not be comprehensive one.

Limitations of the study

The researcher has not deliberately confined his study on this topic in West Belessa. There are some limiting factors which forced him to do so. Among them the most important are:

- The shortage of time and lack of finance made it impossible to make a comprehensive study.
- Due to shortage of materials, this is to mean that, there are no much studies in relation to the identification and characterization of gem agate.
- Since the writer of this paper is also the beginner he should not be expected to present a complete study on the topic controlling all limiting factors.

The researcher believes that this small study will be the screen board and contribute its part for those people who are interested in the further study of this topic

2 LITRATURE REVIEW

Agates have a cryptocrystalline quartz structure formed from microscopic particles, mainly fibrous and partially granular SiO_2 particles, which are mainly chalcedonic silica components Therefore it is classified as a microcrystalline quartz variety [7].

Depending on the type of low-temperature quartz (or silica) polymorphs, microcrystalline quartz structure is classified into two sub-varieties. These polymorphs are cryptocrystalline quartz or pseudo crystalline quartz. Chalcedonic quartz(Ch) is the first sub-variety of microcrystalline quartz in which cryptocrystalline fibrous α-quartz and cryptocrystalline grainy α-quartz are the main components. However, since they produce the same numerical peak data from the XRD patterns the fibrous and grainy phases of micro crystalline quartz are difficult to distinguish from each other using X-ray diffraction. Because of this both phases are lumped together as one silica phase, namely cryptocrystalline α-quartz (chalcedony). However these polymorphs are easily distinguished as fibrous and granular textures which are typical of agate using polarized light microscope Fig. 2(B). In addition, as done by XRD a new silica-polymorph, cryptocrystalline quartzine called moganite (Mo) which often forms as intimately intergrowth with cryptocrystalline α-quartz in many microcrystalline SiO_2 varieties Fig. 3(B). Moganite is the boundary between cryptocrystalline α-quartz silica polymorph and crystalline α-quartz silica polymorph.

A) B)

Fig. 2.A) Two distinct agate's bands: The external is built of fibrous chalcedony and the internal of quartz grains. B) Agate with fibrous-radial and pseudo granular microtexture.[28].

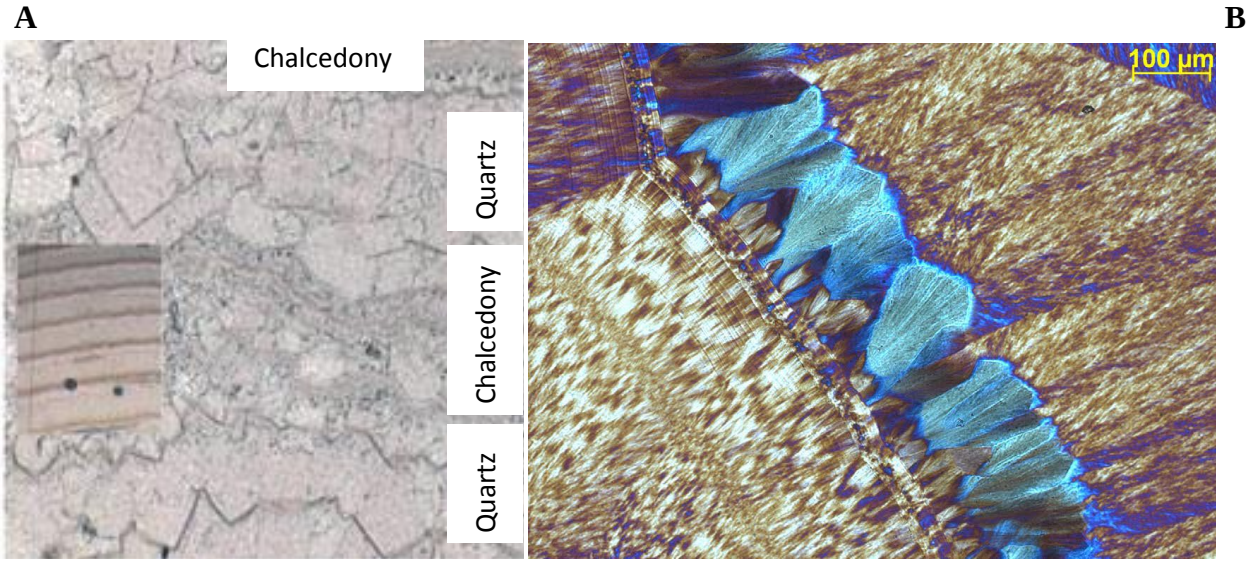


Fig. 3. A) petrographic microscope image in plane-polarized light showing alternating chalcedony and quartz bands[9]. B) Polarized light micrograph showing a quartzine layer (bluish) intercalated between chalcedony layers (yellow) within agate sample [6].

Opaline quartz is the second sub-variety of microcrystalline quartz in which pseudocrystalline cristobalite, and tridymite (called opal-CT and opal-C silica phases) are the principal components [7]. Due to the nano range size of moganite crystallites and its similar structural relationship with α-quartz, the XRD pattern of moganite is quite similar to that of α-quartz this makes difficult to identify moganite in different microcrystalline quartz variety using X-ray diffraction XRD [3]. But the moganite phase is in enough abundance some of its peaks are well observed for the characteristics of moganite phase only, the atomic planes are at $2\theta \sim 19.9$ (011), $2\theta \sim 28.7$ (211), and $2\theta \sim 30.9$ (013) [18, 19].

However, in various Microcrystalline silica the presence of moganite and the relative moganite to quartz ratio are determined by an important tool called Micro-Raman Spectroscopy. Vibration bands of the hydroxyl (OH) group water species, main silica mineral building phase and/or silica inclusions, structural point defects, structural bonds, and coloration in silica are determine by FT-IR patterns in the mid-infrared region. Therefore, the presence of water in gem and other mineral species are mostly confirmed by mid-infrared absorption spectroscopy [20].

Although agates are made up of almost entirely of SiO_2, it also contains trace quantities of various other elements that are responsible for their color and lead to their characteristic banding.

Trace element impurities present outside the fibrous agate structure causes the pigmenting qualities of agates, while the incorporation of trace elements leads to the small-scale, structural banding seen in agates. The composition of trace elements vary widely from place to place, however as many trends that are common to almost all agates of igneous origin shows, both acidic and basic volcanic host agates have similar trace element data [12].

Beside the common elements present in agate with higher concentrations such as Al, Ca, Fe, K, Na, Ge, B and U, it also contains a number of elements with lower concentration. During agate formation, these elements are mobilized from surrounding host rocks, transported and accumulated together with SiO_2 during late and post volcanic alteration processes. Trace elements can be incorporated by substitution of Si and in interstitial positions, or may be present as fluid inclusions and other minerals into the quartz structure. Due to the small number of ions (such as Al^{3+}, Ga^{3+}, Fe^{3+}, Ge^{4+}, Ti^{4+}, and P^{5+}) that have similar ionic radii and valence to substitute Si^{4+} in the crystal structure, the structural incorporation is limited. As shown by several geochemical studies of agates; chalcedony and macro crystalline quartz can be enriched in Al, Fe, Ca and Na, which comes from alteration processes of the volcanic host rocks and the associated release of chemical elements. For example the decomposition of volcanic glass and feldspar provides high amount of Si, Al, Ca, Na and K. In conclusion, the formation of agates are associated with the alteration or weathering of surrounding host rocks and silica transport by residual magmatic fluids (H_2O, but also CO_2 or HF) and/or heated meteoric water. Such processes are evidenced by the chemical composition of the agates and the association with typical secondary minerals such as clay minerals, zeolites or iron oxides [21].

3 MATERIALS AND METHODS

3.1 Instruments, Apparatus, Reagents and Standards

Instrumentation and Apparatus

A refractometer of USA manufacture was used to measure the refractive index with an optical contact liquid of 1.81±0.05 RI at 25^{o}C. By heavy liquid test (Lithium salt with specific gravity 2.57 (USA)), the specific gravity of agate was measured. MOHS HARDNESS PENCILS (USA) instrument was used to determine the hardness value of the agate sample. A Diamond Pacific Machine (USA manufacture) to cut and a diamond paste machine (USA) to polish the agate

sample were used. Agate mortar and pestle was used for pulverizing the agate sample. To sieve the powdered agate sample a sieve with 0.1mm size was used. An electronic digital balance (Denver instrument company, USA) was used to weigh the powdered agate sample. A minflux 600 powder X-ray diffractometre Rigaco (USA) with CuKα radiation (λ=1.5418 Å) and graphic monochromator in the range of 2 θ, 10 to 70^{o} was used for recording the diffraction pattern of agate sample. A 65 FT-IR spectrometer PerkinElmer (U.S.A), operated at transmittance mode in the range of 4000-400 cm^{-1} with 4 cm^{-1} nominal resolution and the average scanning speed of 4 mm/sec was used for recording the infrared transmission spectra using the KBr pellet method. Porcelain crucibles and hot plates were used to digest the agate sample. The pipettes (1 mL, 2 mL, 5mL, and 10mL, 100 mL, and 250 mL), graduated cylinders and beakers were used to dilute the standards and sample. An atomic absorption spectrophotometer (Buck model 210 VGP, USA) equipped with air/acetylene flame, with a hollow cathode lamp for the determination of Magnesium, Calcium, Iron, Copper, and Manganese were used.

Chemicals and Standard Solutions

Chemicals that were used in the analysis are analytical grades: KBr (65 FT-IR spectrometer PerkinElmer (U.S.A) accessories and consumable kit), 69-72% HNO_3 (WINLAB LIMITED MAIDENHEAD-BERKSHIRE-UNITED KINGDOM), Assay (acidimetric) 35.38% HCl (Blulux®, LABORATORY REAGENT, Blulux Laboratories (p) Ltd-121001), 48% HF (Anala R, IMO: Hydrofluoric acid Solution BDH Laboratory supplies, England), and 30% w/v H_2O_2 (CDH Laboratory Reagent, Central Drug house (p) LTD., New Delhi). Stock standard solutions of the metals Ca (1000 μg/mL), Fe (1000 μg/mL), Mn (1000 μg/mL), Mg (1000 μg/mL), and Cu (1000 μg/mL) were used for the preparation of calibration curves for the determination of metals in the sample by atomic absorption spectrophotometer (Buck model 210 VGP, U.S.A.). Deionized water was used for cleaning of glassware and dilution of sample and standard solutions.

3.1.1 Collection of agate sample

Agates were received from Lapidary department of Gondar Polytechnique college, North Gondar, Gondar (Fig. 4). Samples are gem Agate, and come from volcanic or sedimentary environments. Their body color spans almost white gray and they have irregularly shaped banding with crystalline quartz filling in the center of the agate nodule. Analyses were done on the sample.

Fig. 4. The natural gem Agate sample from West Belessa

3.1.2 Sample Preparation

Based on the procedure that was employed [22], after the sample were crushed with a diamond pacific machine and polished with a diamond paste, the sample were washed with deionized water, air dried and ground in to a fine powder using agate mortar and pestle and then sieved with a 0.1 mm sieve. The FTIR analyses, exactly 1 mg (using electronic digital balance) of the agate sample in 250 mg KBr were prepared to make circular pellets. The XRD analyses were performed by taking fixed mass of sieved powder sample. For the FAAS analysis, 0.5 g agate powdered sample prepared from the above sample preparation method were put into porcelain crucibles and 5 mL conc. 69-72 % HNO_3, 2 mL 35.38 % HCl, 1 mL 30 % w/v H_2O_2 and 2 mL of 48 % HF were added. On a hot plate crucibles were heated and the solution evaporated to near dryness. Then until precipitate of SiO_2 is eliminated as SiF_4 vapors, 2 mL 48 % HF were added few times. The sample were allowed to cool to room temperature, 2 mL conc. HCl and 5 mL deionized water were added then filtered through Whatman no. 42 filter paper and diluted to 50 mL volumetric flasks with deionized water .

3.2 Physical Measurements

3.2.1 Determination of Gemmological Properties

In order to verify that the sample were indeed agate, some basic gemmological (non-destructive) identification tests; refractometer of USA manufacture with an optical contact liquid of 1.81±0.05 RI at 25^{o}C, specific gravity using heavy liquid method (Lithium salt) and the instrument "MOHS HARDNESS PENCILS" were performed to measure the refractive index, specific gravity and hardness of the sample found from West Belesa, respectively. The tests were carried out in Lapidary department of Gondar Polytechnique College, Gondar.

3.2.2 Characterization using XRD

To analyze the agate sample by XRD, the sample were cut using diamond pacific machine and polished using diamond paste machine and powdered into fine particles using agate mortar and pestle. The powder was sieved using a 0.1 mm sieve and air dried to remove the moisture content. Then XRD measurements were carried out using a minflux 600 powder X-ray diffractometre Rigaco (USA) with CuKα radiation (λ=1.5418Å) and graphic monochromator. Random amounts of finely powdered agate sample were scanned at a rate of 1^{o}/min in the range of 2 θ, 10 to 70^{o} for identification of the mineral phases that were present. The result was collected in Addis Ababa University.

3.2.3 Characterization using FT-IR

The instrument's total inspection was done by measuring absorbance of the standard polystyrene film and empty sample compartment turn by turn before the sample were run in 65 FT-IR spectrometer PerkinElmer (U.S.A). A back ground (KBr) measurement was done.

To analyze the agate sample using FT-IR, the sample were cut using diamond pacific machine and polished using diamond paste machine, air dried and powdered into fine particles using agate mortar and pestle. The powder was sieved using a 0.1 mm sieve. The fine powders were weighed using electronic digital balance and mixed with 250 mg KBr powder. The mixture were powdered further so as to mix well and then put in a sample holder of the instrument for solid sample. The sample was examined by 65 FT-IR spectrometer PerkinElmer (U.S.A), operated at transmittance mode in the range of 4000-400 cm^{-1} with a 4 cm^{-1} nominal resolution and the

average scanning speed of 4 mm/sec for the sample and background. The spectra were collected in chemistry department of Addis Ababa University.

3.2.4 Trace metal determination using FAAS

For the FAAS analyses, several parameters such as burner head position (vertical, horizontal) and flow rate of used gases are a function of the absorbance of an analytic line. These parameters which yield maximum absorbance value are optimal values. The optimization procedure was carried out by studying the effect of one parameter while keeping the others constants at appropriate values. To carry out this study the acetylene and airflow rate were kept constant.

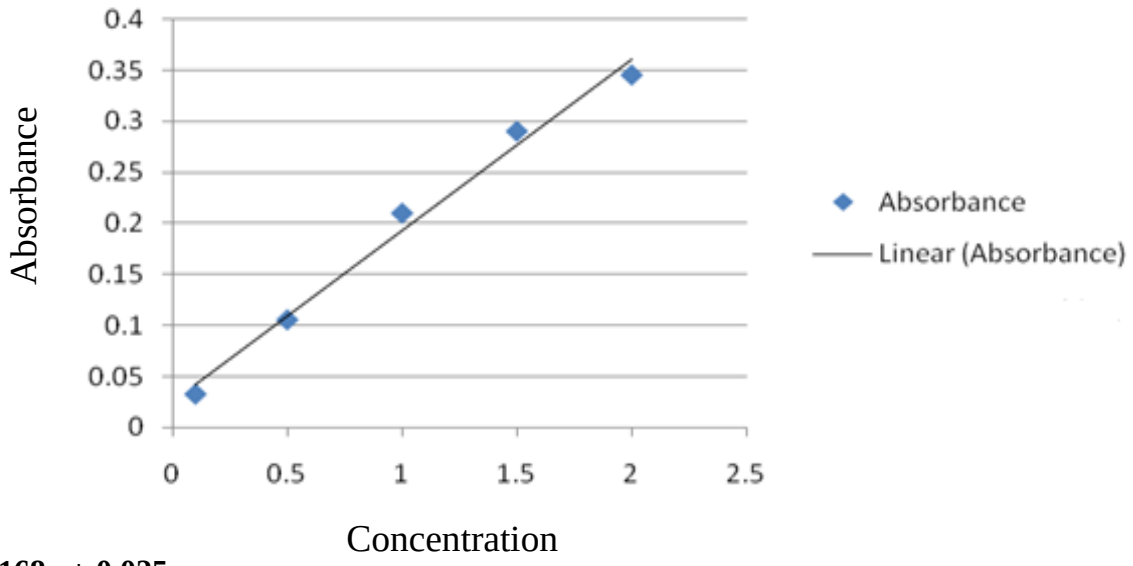
Five series of standard metal solutions (Table 1) were prepared by diluting the stock solutions of the metal with deionized water for the determination of metals in West Belessa agate. A blank (deionized water) and standards were run in flame atomic absorption spectrophotometer (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) and five points of calibration curve were established. Sample solutions were each aspirated into the FAAS instrument and direct readings of the metal absorbance were recorded. Three replicate determinations were carried out for the sample. For each analyte the employed operating conditions of FAAS are given in Table 2.

Table 2.Series of working standards for determination of trace metals in Agate sample

No	Element	Concentration of standards in μg/mL	Correlation coefficient (R)
1	Mn	0.1, 0.5, 1, 1.5, 2	0.919
2	Fe	1, 3, 5, 7, 9	0.960
3	Mg	0.5, 1, 1.5, 2, 2.5	0.958
4	Ca	0.5, 1, 1.5, 2, 2.5	0.808
5	Cu	0.1, 0.5, 1, 1.5, 2	0.991

Table 3. Instrumental operating conditions for determination of metals using Flame Atomic Absorption spectrometer.

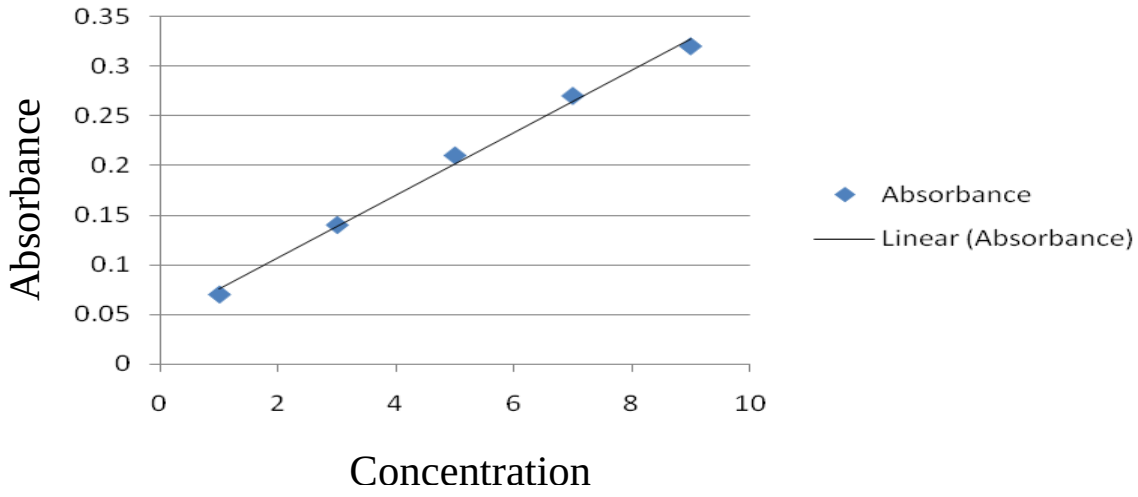
Elements	Wave length (nm)	Current (mA)	Slit width (nm)	Detection limit (mg/L) from the instrument's operator manual	Energy (J)
Mn	279.5	3	0.7	0.03	4.253
Fe	248.3	7	0.2	0.05	3.844
Mg	285.2	1	0.7	0.005	4.501
Ca	422.7	2	0.7	0.05	0.990
Cu	324.7	1.5	0.7	0.01	3.869



Y = 0.168x + 0.025

R^2 = 0.987

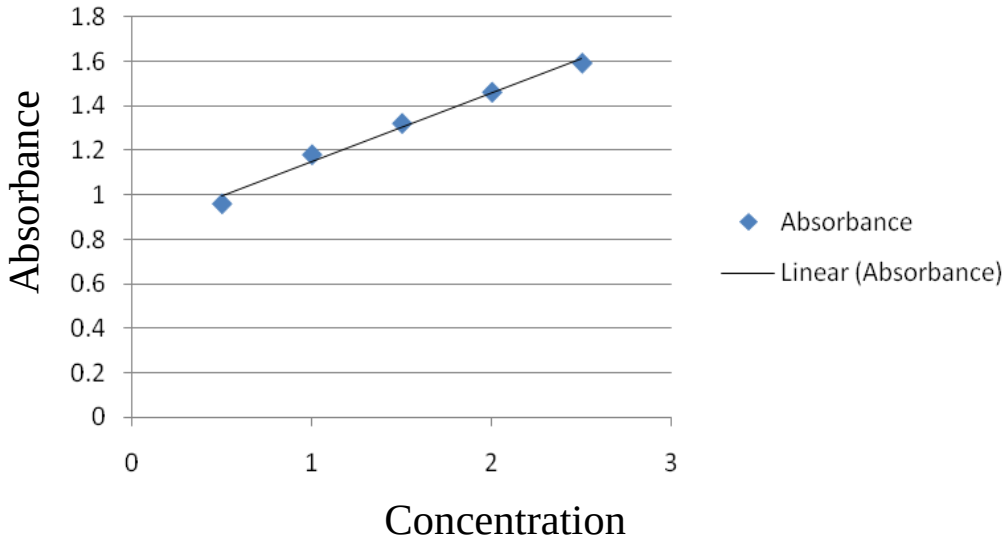
Fig. 5. Calibration graph for manganese standard solution



y = 0.031x + 0.044

R^2 =0.995

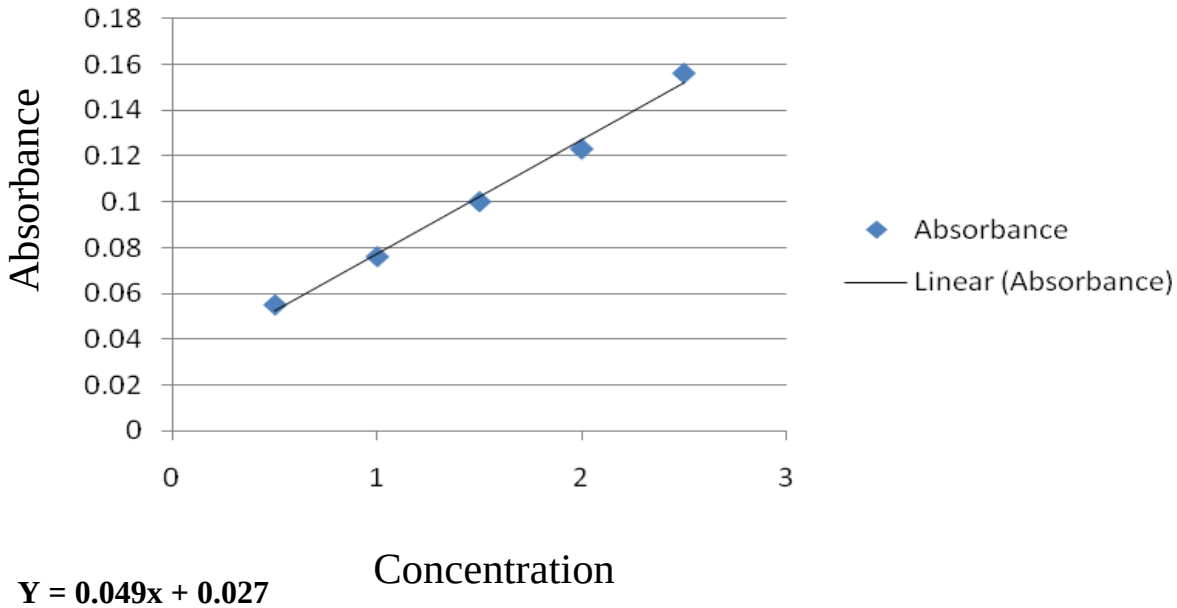
Fig. 6. Calibration graph for Iron standard solution



Y =0.308x +0.84

R^2 =0.987

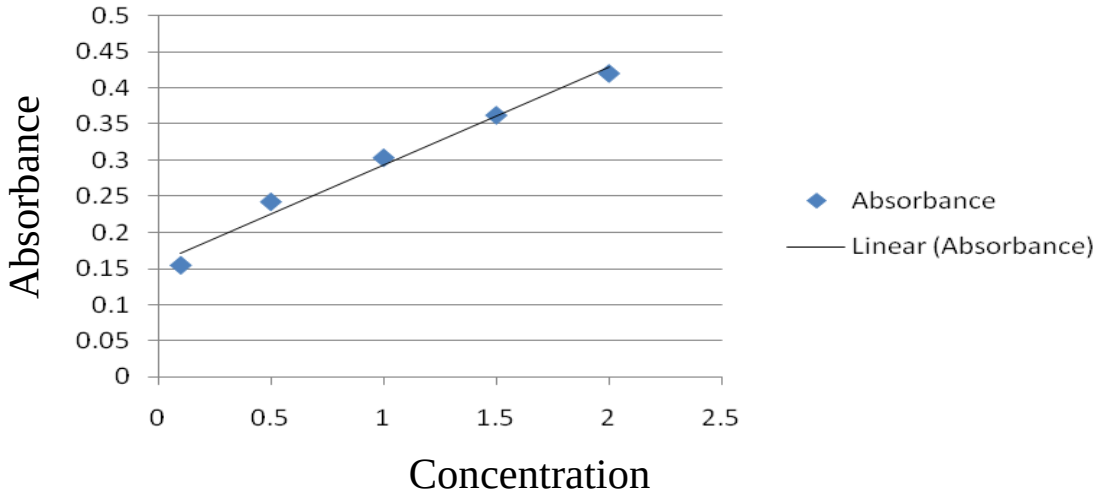
Fig. 7. Calibration graph for magnesium standard solution



Y = 0.049x + 0.027

R^2 = 0.992

Fig. 8. Calibration graph for calcium standard solution



Y=0.135x + 0.158

R^2 = 0.982

Fig. 9. Calibration graph for copper standard solution

4 RESULTS AND DISCUSSION

4.1 Gemmological properties

The gemmological properties of agate sample from West Belessa, are given below:

Table 4. Some essential gemmological measurements of agate from West Belessa and its value.

Basic gemmological measurements	Sample value of agate from North Gondar
Hardness	6.5-7
Refractive index (RI)	1.53-1.54
Specific gravity (SG)	2.57-2.62

As seen from the table above; the hardness, refractive index, and specific gravity of agate sample from West Belessa are (6.5-7), (1.53-1.54), and (2.57-2.62) respectively. Moreover, the result shows the Gemmological properties of the representative agate sample are generally consistent with the literature [23,31]. This confirms the sample were indeed agate.

4.2 X-ray diffraction (XRD)

The XRD diffraction pattern of the representative sample of agate collected from West Belessa are presented in Fig. 10. As we see from the spectra triplets (the most intense, moderately intense and less intense) peaks are present in the range of 2θ 10 to 70^{o}. Determination (identification) of microcrystalline silica building phase (such as cryptocrystalline α-quartz called chalcedony (ch), moganite (Mo), opal-CT and opal-C) present in the sample were made by the d-spacing [Å] comparative matching technique [7, 13, 18, 20, 23]. The ideal XRD data of microcrystalline silica phases are compiled from PDF card [25] and from some related previously published papers [7, 18, 20, 23].

The diffraction pattern of agate sample shows that the most intense and moderately intense peaks represents the overlap of chalcedony with those of moganite, and additional reflection for the characteristics of single chalcedony and moganite at the lowest peak were matched with the literature [7, 13, 18, 20, 23] (spectra in the appendix on page 32). Similarly, the peak around

$2\theta\sim$24 were also matched with the literature [30] which represents impurities present in the sample and according to the literature [32] these impurities could be green earth coating celadonite (spectra in the appendix on page 33).

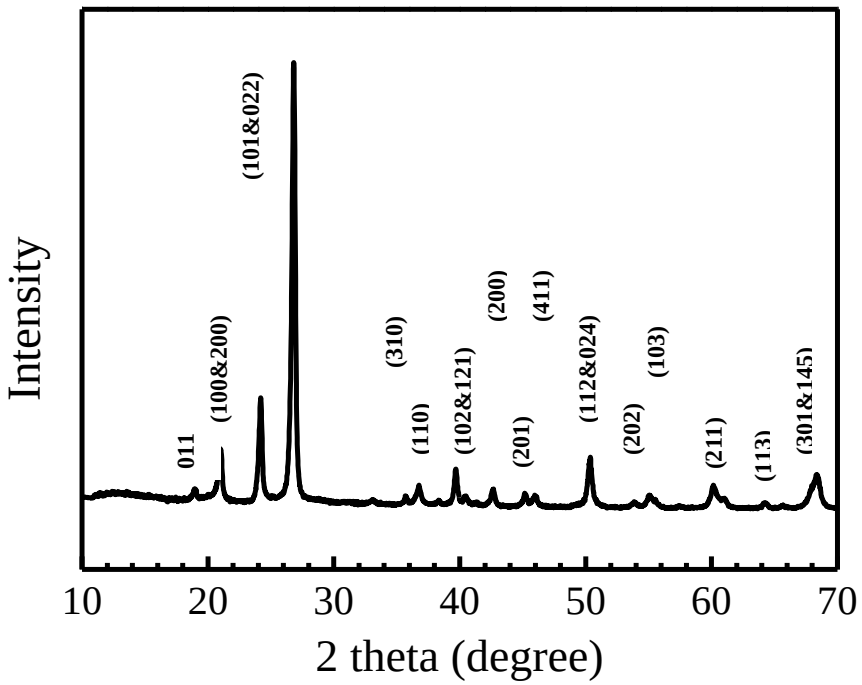


Fig. 10. XRD pattern of Agate from West Belessa.

The result of XRD pattern confirms both cryptocrystalline α-quartz and moganite are present. However opal-CT and opal-C were not found in the investigated sample.

In the investigated agate sample, the atomic plane (hkl) for the overlap of α-quartz and moganite were observed at $2\theta\sim$20.85 (100&200), $2\theta\sim$26.65 (101&022), $2\theta\sim$39.46 (102&121), $2\theta\sim$50.14 (112&024), $2\theta\sim$67.75 (212&-262), and $2\theta\sim$68.13 (301&145), and the atomic plane (hkl) for the characteristics of single α-quartz were observed at $2\theta\sim$36.54 (110), $2\theta\sim$40.29 (111), $2\theta\sim$42.47 (200), $2\theta\sim$54.87 (202), $2\theta\sim$55.33 (103), $2\theta\sim$59.95 (211), and $2\theta\sim$64.00 (113). In addition the atomic plane (hkl) for the characteristics of single moganite phase were present at $2\theta\sim$19.9 (011), $2\theta\sim$35.7 (310).

4.3 Infrared spectroscopy (FT-IR)

The FT-IR spectra of the studied sample of agate found from West Belessa are presented in Fig. 11, from 4000 to 400 cm^{-1}. As seen from the spectra the broad band centered around 3450 cm^{-1} and sharp band near to 3600 cm^{-1} are observed, the frequency of these bands are very similar with the OH stretching vibration band due to free molecular H_2O and silanol group H_2O (Si-OH) present, respectively. The results were inline with the corresponding literature data [9,24]. The result indicates structurally bonded H_2O (Si-OH group) and molecular water as a fluid inclusion are present in the sample.

Going towards the moderate frequency, weak peaks from 1500 to 2000cm^{-1} are observed. The first band around 1870 cm^{-1} could be Si-O vibration whereas the second approximately 1640 cm^{-1} is because of H-O-H bending in water, so the strength of this peak reflects to some extent the content of molecular water in the sample. This is in consistent with the literature [20].

In the literature the frequency of duplets are present at 798 and 779 cm^{-1} in different crystalline quartz samples and only one peak observed at around 780 cm^{-1} in opal sample [22]. Similarly duplets are present at 775 and 795 cm^{-1} in chalcedony [20], look the spectra in the appendix on page 31.

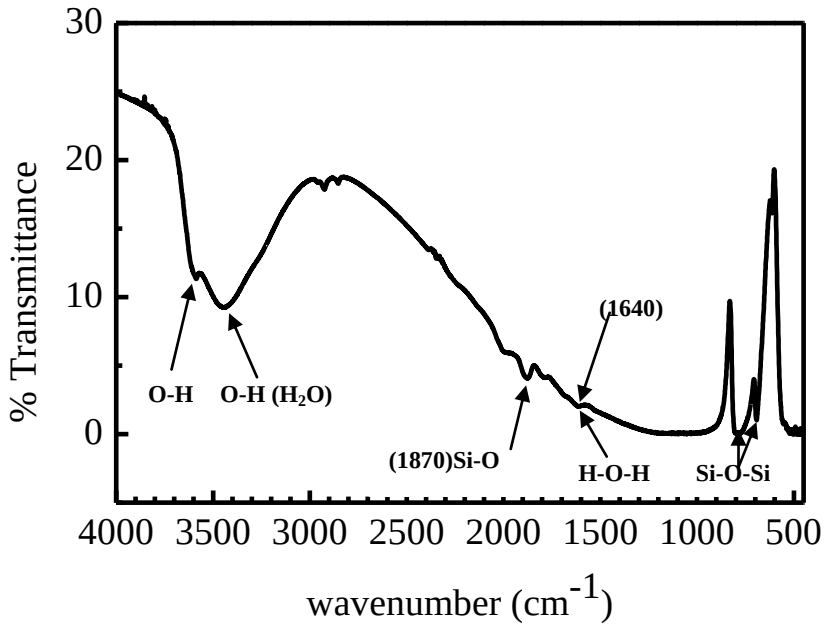


Fig. 11. FT-IR spectroscopy spectra of Agate from West Belessa

Going towards the lower frequency duplets are observed in the representative agate sample around 800 cm^{-1} (Fig. 11), this indicates the sample may contain either crystalline quartz only or micro crystalline quartz only, or both quartz varieties. However, the spectra around 3450 and 3600 cm^{-1} is in consistent with the literature [9, 26] that contains broad band and sharp peak for the presence of molecular H_2O and silica Si-OH in microcrystalline quartz. In addition, the lack of IR response for water (molecular H_2O and Si-OH group) in crystalline quartz only [9, 26] indicates the main silica building phase of the studied agate is microcrystalline quartz.

In conclusion, since the physical appearance of agate shows layers with crystalline quartz center, this agate contains mainly microcrystalline quartz with inner crystalline quartz. And the duplets around 800 cm^{-1} could be Si-O-Si inter tetrahedral bridging bond present in silica building phase of agate. This is in consistent with the literature [27].

4.4 Flame Atomic Absorption spectroscopy (FAAS)

The content of trace elements determined using FAAS of the investigated agate are present in table (5). As seen from the table Mg, Ca and Fe are the most abundant whereas the concentration of other elements is very small.

Some elements are usual implication for coloration (pigmenting agent) and genesis. Rock forming elements such as Al, Ca, Mg, K, Sr, and Be are mobilized together with silica during hydrothermally dissolving, transporting and accumulating throughout volcanic host rock [23]. The high content of Mg and Ca in the sample suggested that these elements may be mobilized together with silica during alteration of the volcanic host rock.

Table 5. Mean concentration ($\bar{x}$ ± SD, n = 3, mg/g dry weight) of impurity and trace element contents of West Belessa agate

Sample type	Concentration of Metals (mg/g)				
Agate	Fe	Mn	Mg	Ca	Cu
	15.27±3.84	0.07±0.086	2.15±0.22	9.99±0.69	0.48±0.29

$\bar{x}$=mean SD = standard deviation

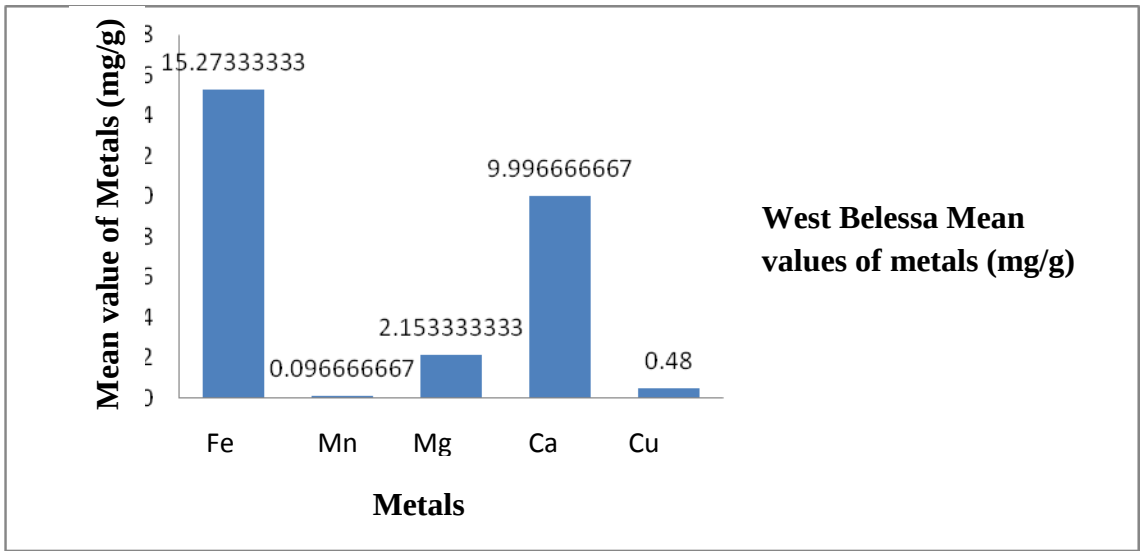


Fig. 12. Histogram comparing mean concentrations (n = 3, mg/g, dry weight) of metals in West Belessa Agate.

Transition elements such as Fe, Mn, and Cu are present in the investigated agate sample. In fact these elements are well known pigmenting agent in the mineral variety. It was observed that the red color of agate is correlates with the presence of Fe while Ca leads to the milky colored sample.

5 CONCLUSION

Gem quality agate of West Belessa, North Gondar, Ethiopia, has not previously been studied at all. Therefore, some interesting conclusions are available for the first time from this study.

According to XRD results it is detected that agates found in West Belessa, North Gondar contains two important microcrystalline silica phase. These are microcrystalline α-quartz (Ch) and moganite (Mo). However, these agates do not include other important opaline silica phases of microcrystalline structure, such as (opal-CT and opal-C). FT-IR spectra indicate the presence of free H_2O molecular and structurally bonded silanol Si-OH group as defect site. Significant concentrations of Ca, Mg and Fe in the sample suggest that the formation of agate from West Belessa was affected by the decomposition of volcanic glass and feldspar.

In conclusion, Agates found in West Belessa are almost similar with worldwide agates found, such as Turkey in terms of main silica building phases such as microcrystalline α-quartz and moganite, however some trace element concentration data presented here are in lower content with other published values.

6. RECOMMENDATION

In fact it's possible to state gemstone technology in Ethiopia is a recent phenomena and it's very surprising and irritating in comparison with other countries in this technology. To clearly state, we have abundant gemstones but not still in manner in exploiting and benefited from those minerals. The researcher of this particular study suggests the following causes of action to be taken:

- Those concerned body's such as researchers and chemists should be made vigorous effort and further work on study in creating awareness in Gemstone technology and gem quality agate of West Belessa societies.
- Further work should be on investigating gem quality agate and promoting its contribution to society and industrialization and supply market.
- It's not only researchers but those concerned bodies (i.e chemists, geologist, and gemologists) should expect to made vigorous effort and further work in exploring, identifying and characterizing gem quality agate of West Belessa.

- The last but not least, the researcher of this study strongly argued and suggests there should be made vigorous effort and aggressively works on promoting the gem stone quality agate. In addition to this, it should be made vigorous effort and work on preserving and/or treating this gem quality agate of the area and increasing its contribution of supply market of industry and to faster the country's economy through gem stone technology.

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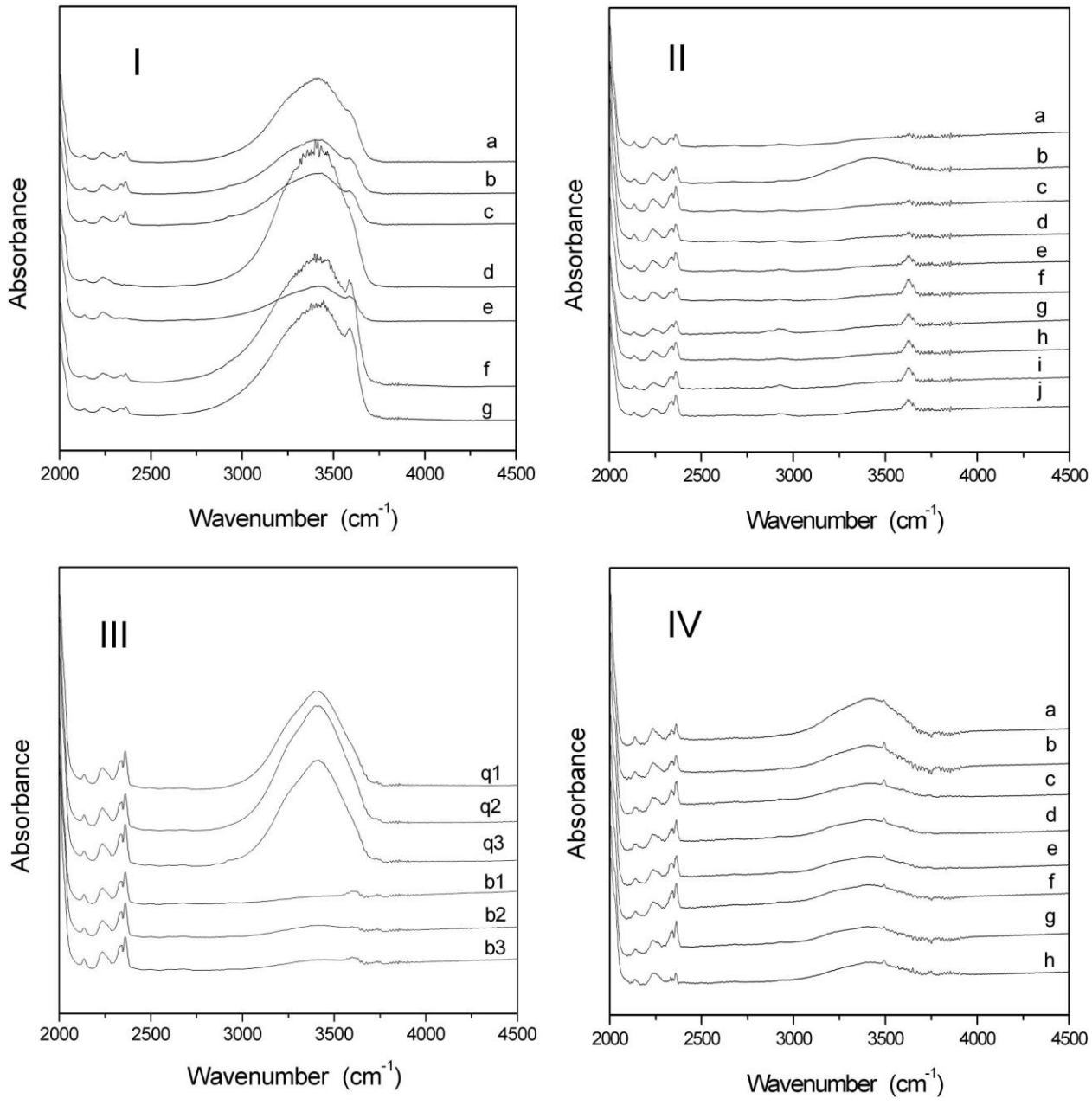
8. APPENDICES

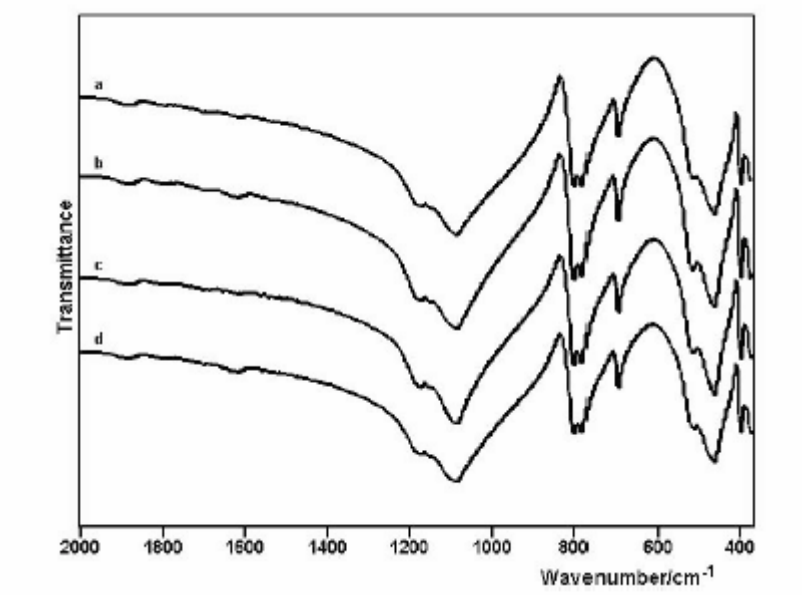
APPENDIX A. FT-IR Spectra of different agate samples and quartz varieties from different countries of different literatures.



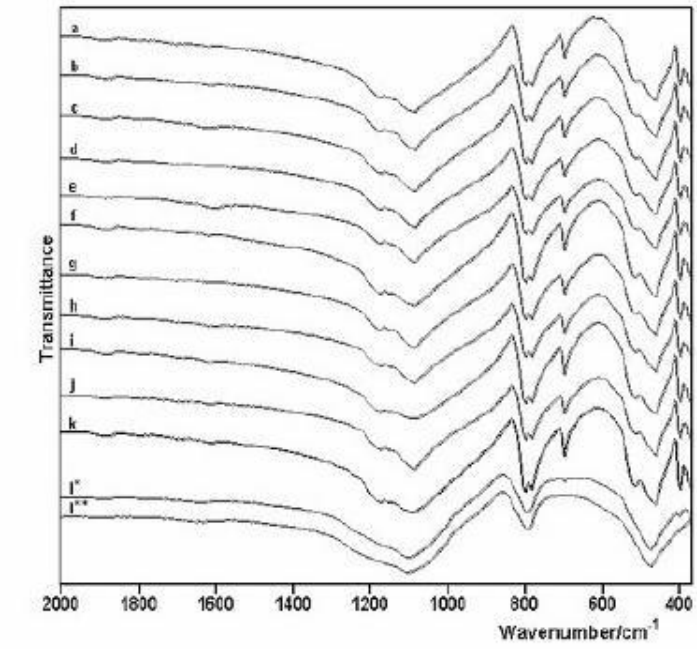
[27]

I. a,b,c (United State), d,e (Scotland) and f,g (Mexico) II. a,c,d (Western Australia)

III. q1, q2, q3 and b1, b2, b3 (Western Australia) IV. a—h, (Western Australia)

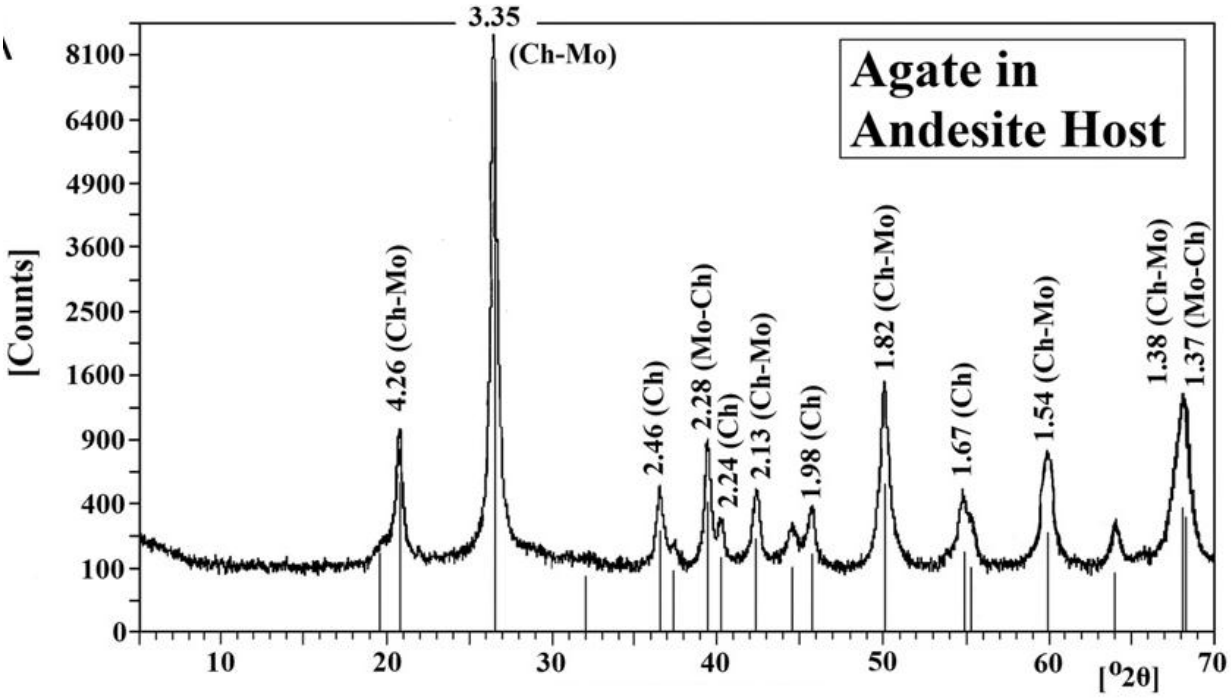


[**22]**

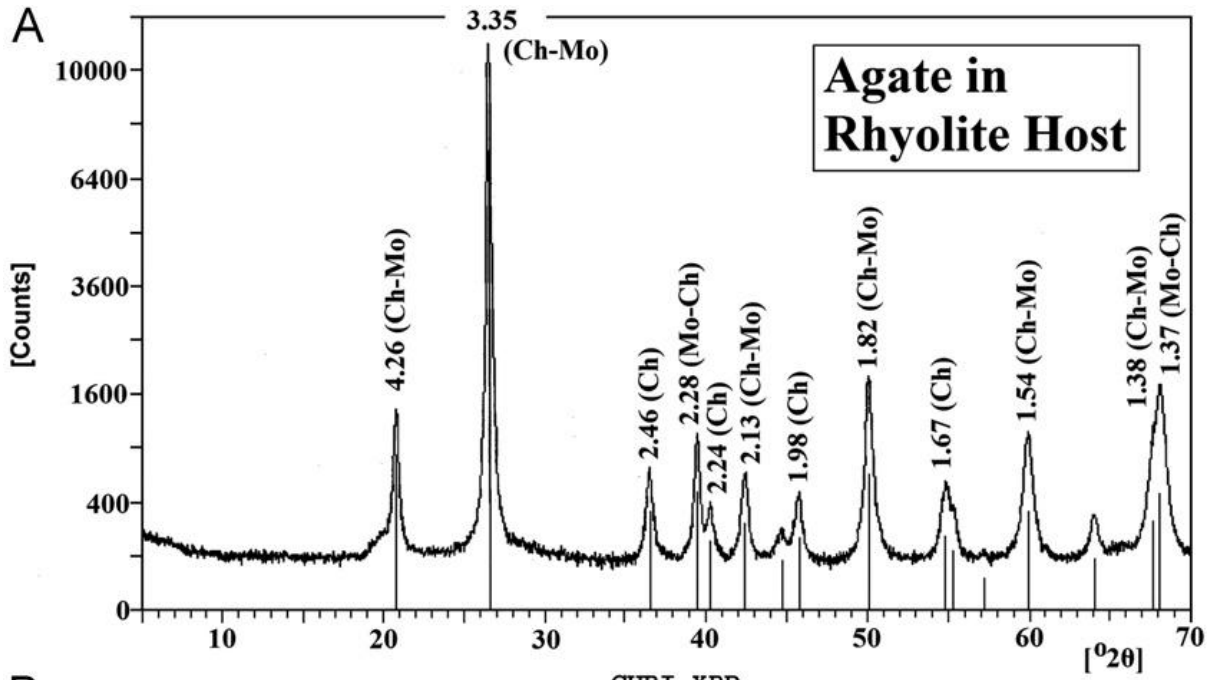


[22] Opal and crystalline quartz varieties of republic of Macedonia.

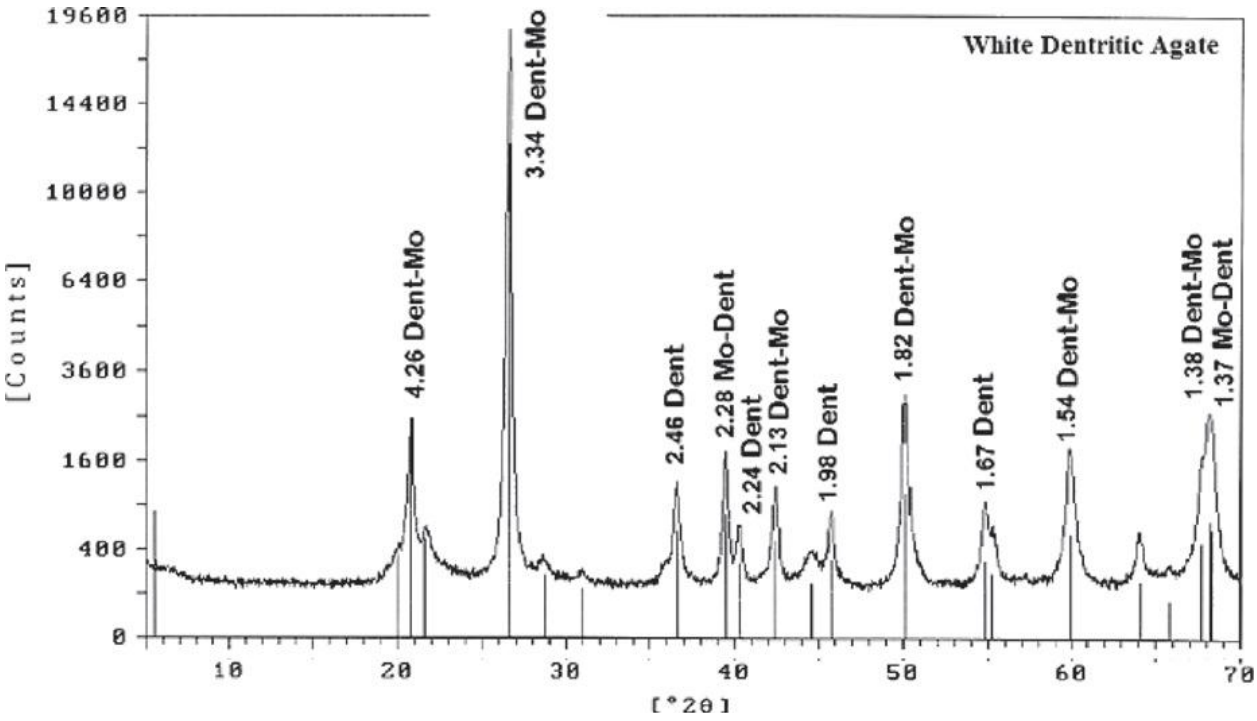
APPENDIX B. XRD pattern of different agate samples and quartz varieties from different countries of different literatures.



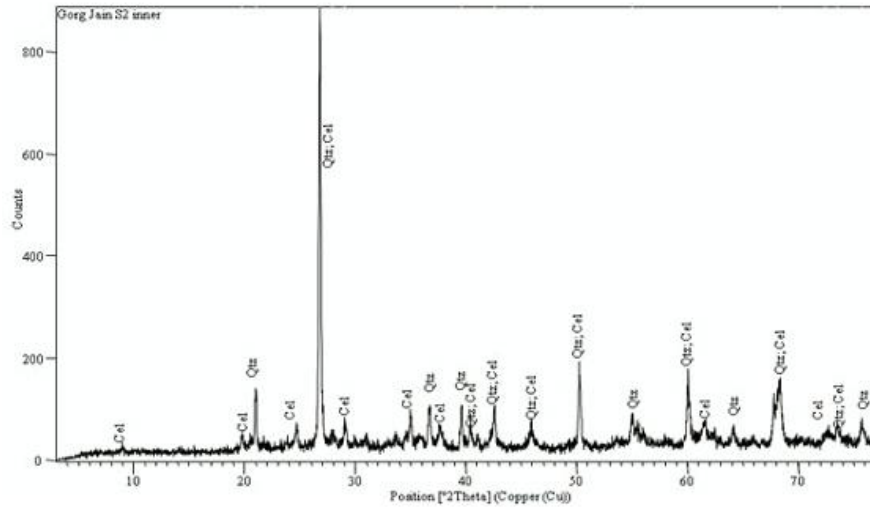
[13]



[13] Turkey agates



[5] Turkey agate



[32] Botswana agate